FREE ENERGY & SPONTANEITY

Free Energy (G)

- A thermodynamic function whose value describes whether or not a process is spontaneous
  - Dependent on ΔH, ΔS, and temperature:

$$\Delta G = \Delta H - T\Delta S$$

- Can predict spontaneity based on ΔH and ΔS's signs

ΔS	ΔH	ΔG
+	-	Spontaneous
+	+	Spontaneous at high temperatures
-	-	Spontaneous at low temperatures
-	+	Not spontaneous

Free Energy and Chemical Reactions

- Free energy is a state function and therefore can also be standardized at 25°C and 1 atm

$$\Delta G° = \Delta H° - T\Delta S°$$

  - ΔG can be calculated from ΔH and ΔS
  - Also temperature at which spontaneity will occur can also be calculated

- Can also be calculated as

$$\Delta G°_{reaction} = \sum \Delta G°_{products} - \sum \Delta G°_{reactants}$$

Example #1

- Consider the reaction, 2 SO_2 (g) + O_2 (g) $\rightarrow$ 2 SO_3 (g), carried out at 25°C and 1 atm. If $\Delta H°$ is -198 kJ and $\Delta S°$ is -187 J/K, calculate $\Delta G°$.

$$\Delta G° = \Delta H° - T\Delta S°$$

$$\Delta G° = (-198\ kJ) - (298\ K)\left(-187\frac{J}{K}\right)\left(\frac{1\ kJ}{1000\ J}\right)$$

$$= -142\ kJ$$

Example #2

- Consider the reaction: 2 $POCl_3$ (g) → 2 PCl_3 (g) + O_2 (g). The value of $\Delta S°$ is 179 J/K. The value of $\Delta H°$ is 542 kJ. At what temperature is this reaction spontaneous?

- For a spontaneous reaction, $\Delta G° \geq 0$, so

$$\Delta G° = \Delta H° - T\Delta S° = 0; T = \frac{\Delta H°}{\Delta S°}$$

$$T = \frac{542\ kJ}{0.179\frac{kJ}{K}} = 3030\ K$$

Free Energy and Pressure/Concentration of Species

- Free energy depends on pressure or concentration of species in a reaction

$$\Delta G = \Delta G° + RT \ln Q$$

  - ΔG is change of free energy for specific pressures and/or concentrations
  - $\Delta G°$ is change of standard free energy
  - Q is the reaction quotient
  - R = 8.314 J/Kmol

Example #3

- One method of synthesizing methanol (CH_3OH) involves reacting carbon monoxide and hydrogen gases: CO (g) + 2 H_2 (g) $\rightarrow$ CH_3OH (l). Calculate the ΔG at 25°C for this reaction where carbon monoxide gas at 5.0 atm and hydrogen gas at 3.0 atm are converted to liquid methanol and $\Delta G°$ is -2.9 x 10^4 J/mol.

$$\Delta G = \Delta G° - RT \ln Q$$

$$Q = \frac{1}{(P_{CO})(P_{H_2})^2}$$

$$\Delta G = -2.9\ x\ 10^4 \frac{J}{mol} - \left(8.314 \frac{J}{Kmol}\right)(298\ K) \ln\left(\frac{1}{(5.0)(3.0)^2}\right)$$

$$= -38 \frac{\text{kJ}}{\text{mol}}$$

Free Energy and Equilibrium

- If the reaction is at equilibrium then ΔG is zero
  - Therefore:

$$\Delta G^\circ = RT \ln K$$

    - K is equilibrium constant
    - R = 8.314 J/Kmol

Example #4

- Calculate the value of K at 25°C for the reaction

$$2\ NO_2\ (g) \leftrightarrow N_2O_4\ (g)$$

The values of $\Delta H°$ and $\Delta S°$ are -58.03 kJ/mol and -176.6 J/Kmol, respectively.

- First have to calculate $\Delta G°$

$$\Delta G° = \Delta H° - T\Delta S°$$

$$\Delta G° = \left(-58.03\ x\ 10^3 \frac{J}{mol}\right) - (298K)\left(-176.6 \frac{J}{Kmol}\right)$$

$$= -5.4\ x\ 10^3\ J/mol$$

Example #4

$$\Delta G^\circ = RT \ln K \; ; \; \ln K = \frac{\Delta G^\circ}{RT}$$

$$\ln K = \frac{-5.4 \; x \; 10^3 \frac{J}{mol}}{\left(8.314 \frac{J}{Kmol}\right)(298 \; K)} = 2.18$$

$$e^{\ln K} = e^{2.18}$$

$$K = 8.8$$